

(19)



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



EP 1 635 087 A1

(12)

**EUROPEAN PATENT APPLICATION**  
published in accordance with Art. 158(3) EPC

(43) Date of publication:  
15.03.2006 Bulletin 2006/11

(51) Int Cl.:  
*F16G 13/06* (1968.09)      *C23C 10/36* (1985.01)

(21) Application number: 04745476.4

(86) International application number:  
PCT/JP2004/007511

(22) Date of filing: 01.06.2004

(87) International publication number:  
WO 2004/109153 (16.12.2004 Gazette 2004/51)

(84) Designated Contracting States:  
DE FR GB IT

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(30) Priority: 03.06.2003 JP 2003158075

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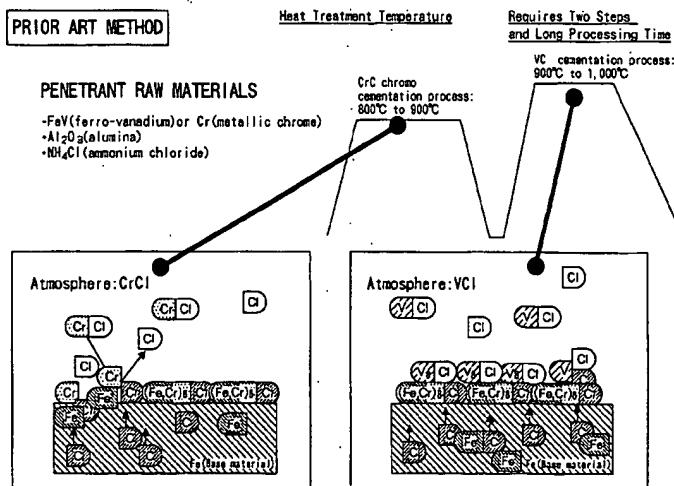
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**(54) PIN FOR CHAIN AND METHOD FOR MANUFACTURE THEREOF**

(57) A chain pin manufacturing method of the invention requires only one heat treatment step of forming a boundary part composed of (V, Cr)<sub>8</sub>C<sub>7</sub> by Cr and C in a base material at first through a cementation process in a VC1 atmosphere by using Cr-rich steel as the pin base material and of forming a surface layer composed of V<sub>8</sub>C<sub>7</sub>. A Cr content in the boundary part decreases gradually toward the base material and the surface layer and

the boundary part is not clearly divided. Accordingly, as compared to a conventional chain pin manufacturing method which has required two steps of heat treatment of forming an intermediate layer by a chrome carbide layer and of forming a surface layer as a mixed layer of vanadium and chrome carbide layers, the inventive manufacturing method is simple and enables to manufacture the pin having high abrasion resistance and suitably used in a severe environment like a timing chain.

FIG.1



**Description****Technical Field**

**[0001]** The present invention relates to a pin for use in a power transmission chain such as a silent chain and a roller chain and more specifically to a chain pin suitably used especially for a chain used in an engine and to a manufacturing method thereof.

**Background Art**

**[0002]** Generally, a relative revolutionary sliding movement occurs between a pin and a link plate in case of a silent chain and between a pin and a bush in case of a roller chain, thus causing abrasion of the pin. Then, various surface treatments have been implemented on the surface of the pin in order to reduce such abrasion.

**[0003]** Conventionally, as a pin whose surface is treated, there have been known a pin in which a chrome carbide layer is formed on the surface thereof (referred to as a chromizing pin hereinafter) and a pin in which a vanadium carbide layer is formed on the surface thereof (referred to as a VC pin hereinafter). Because there are cases when the chromizing pin causes peeling at the surface of the chrome carbide layer and when the VC pin causes peeling at the boundary surface between the vanadium carbide layer and a base material (raw material of the pin) under a use environment in which high surface pressure is repeatedly applied, it is considered that resistance of chrome carbide to surface pressure is low even though its adhesion (binding quality) with the base material is good and that resistance of vanadium carbide to surface pressure is high even though its adhesion with the base material is low.

**[0004]** Then, based on the result of the above consideration, Japanese Patent Laid-open No. 2002-195356 has proposed a method of forming a chrome carbide layer on the surface of a pin base material made from steel by carrying out a chrome cementation process and of forming, thereon, a mixed layer which is thicker than the above-mentioned chrome carbide layer and which contains vanadium carbide as its main component and a small amount of chrome carbide by carrying out a vanadium cementation process at temperature higher than that of the chrome cementation process for the purpose of improving the abrasion resistance under high surface pressure.

**[0005]** However, the pin proposed as described above has had a problem that because the chrome and vanadium cementation process has to be carried out after carrying out the chrome cementation process at the temperature higher than that of the chrome cementation process, it has been cumbersome and costly to carry out such surface treatments.

**[0006]** Especially, in case of a timing chain or the like to which high surface pressure is applied under a high temperature environment within an engine, the surface

pressure resistance of the outermost surface of the pin is not enough as compared to one composed of vanadium carbide ( $V_x Cy$ ,  $V_8C_7$  for example) because it is formed of the mixed layer of vanadium carbide and chrome carbide [ $(V, Cr)xCy$ ,  $(V, Cr)_8C_7$  for example]. Thus it may cause peeling on the surface and abrasion thereof may advance with the advance of peeling. Still more, because a clear intermediate layer composed of the chrome carbide layer exists between the chrome and vanadium mixed layer and the steel, i.e., the base material, there is a possibility of causing peeling at the boundary surfaces between the intermediate layer and the mixed layer, i.e., the upper layer thereof, and between the intermediate layer and the steel base material, i.e., the lower layer thereof, causing quick abrasion as a result.

**DISCLOSURE OF INVENTION**

**[0007]** Accordingly, it is an object of the invention to provide a chain pin and a manufacturing method thereof that solve the above-mentioned problems by forming compound carbide in which chrome content changes in gradient and no clear interface is formed between a base material of the pin and a surface layer composed of vanadium carbide. According to a first aspect of the invention (see FIGS. 4a, 4b and 4c for example), an inventive chain pin is characterized in that compound carbide of vanadium and chrome [ $(V, Cr)xCy$ ,  $(V, Cr)_8C_7$  for example] exists in a boundary part (5) between a pin base material (1) and a surface layer (6) composed of vanadium carbide ( $V_x Cy$ ,  $V_8C_7$  for example) and that the content of chrome (Cr) in the compound carbide decreases gradually toward the surface layer.

**[0008]** According to a second aspect of the invention (see FIG. 3 for example), an inventive manufacturing method of a chain pin is characterized in that steel containing chrome by 0.6 [%] or more is used as a pin base material (1) and a cementation process is carried out on the pin base material (1) at predetermined temperature within a gaseous atmosphere containing vanadium (VC1 for example) to form, at first, compound carbide of vanadium and chrome ( $(V, Cr)_8C_7$  for example) on the surface of the pin base material (1) by chrome (Cr) and carbon (C) supplied from the pin base material (1) and vanadium (V) within the atmosphere, and then to form a surface layer composed of vanadium carbide ( $V_8C_7$  for example) by vanadium (V) within the atmosphere without forming an interface (8) between the surface layer (6) and the compound carbide in a condition in which the supply of chrome (Cr) from the pin base material (1) decreases.

**[0009]** Preferably, the cementation process in the manufacturing method of the chain pin in the second aspect of the invention (see FIG. 3 for example) includes a powder pack method using powder containing vanadium [ferro-vanadium (FeV) for example], a sintering stopping agent [alumina ( $Al_2O_3$ ) for example] and an accelerator [halide such as ammonium chloride ( $NH_4Cl$ )] and the

temperature of the heat treatment is set at 1,000 [°C] to 1,100 [°C].

[0010] While the reference characters have been appended above in the parentheses for the purpose of making a reference to the drawings, it is noted that they will by no means affect the composition of the appended claims.

[0011] According to the first aspect of the invention, the surface layer (6) is composed of the vanadium carbide and has high face pressure resistance, so that it is possible to prevent peeling from occurring on the surface even in a severe use condition in which high face pressure is repeatedly applied at high temperature. Further, the compound carbide of vanadium and chrome is formed at the boundary part between the surface layer (6) and the pin base material (1) without forming distinct interfaces, so that it is possible to enhance the adhesion strength of the surface layer (6) with the pin base material (1) and to prevent peeling from occurring at the interfaces of the compound carbide, the pin base material (1) and the surface layer (6). Thus, it becomes possible to reduce the abrasion of the pin and to prolong the durability and life of the chain even when it is used under a severe use environment.

[0012] According to the second aspect of the invention, the compound carbide of vanadium and chrome is formed at first on the surface of the pin base material (1) and then the surface layer (6) composed of vanadium carbide is formed without forming an interface with the layer of compound carbide through the cementation process based on one step of heat treatment without using two or more penetrants by using the chrome-rich steel as the pin base material, so that the high precision chain pin may be manufactured by one step of heat treatment readily and steadily at low cost.

[0013] Still more, according to the second aspect of the invention, the chain pin may be manufactured accurately without increasing the cost so much by carrying out one step of heat treatment at the temperature of 1,000 [°C] to 1,100 [°C] by the powder pack method having actual results.

#### BRIEF DESCRIPTION OF DRAWINGS

[0014]

FIG. 1 is a chart showing a conventional manufacturing method of a chain pin (as proposed in Japanese Patent Laid-open No. 2002-195356).

FIG. 2 is a schematic diagram showing the structure of a coating film of the conventional chain pin obtained from a sectional photograph.

FIG. 3 is a chart showing an inventive manufacturing method of a chain pin.

FIGs. 4a, 4b and 4c are schematic pictorial views showing sections of the inventive chain pin, wherein FIG. 4a is a schematic pictorial view showing the structure of a coating film obtained from a sectional

photograph, FIG. 4b is a schematic pictorial view showing the structure of the coating film analyzed from the analytical result and FIG. 4c is a schematic pictorial view of the section of the coating film.

FIGs. 5a and 5b are graphs showing the analytical results of the inventive chain pin analyzed by an X-ray probe analyzer, wherein FIG. 5a shows a vanadium content and FIG. 5b shows a chrome content.

FIG. 6 is a graph showing the results of scratch test.

#### BEST MODE FOR CARRYING OUT THE INVENTION

[0015] A mode for carrying out the invention will be explained below with reference to the drawings. An inventive chain pin is applicable to all kinds of power transmission chains such as publicly known roller and silent chains and is suitably applicable to a chain used within an engine such as a timing chain in particular.

[0016] A roller chain is constructed by endlessly connecting pin links in which both ends of two pin link plates are connected by pins with roller links in which both ends of two roller link plates are connected similarly by bushes by fitting the pins into the bushes and by loosely fitting rollers around the bushes. A silent chain is constructed by endlessly connecting a train of guides composed of a plurality of link plates having guide link plates at the both ends with a train of knuckles having no guide link plate and having only toothed link plates by pins fixed in the guide link plates.

[0017] Then, every time when such chain is wound, a sliding contact movement occurs between the pin and the bush in case of the roller chain and between the pin and a pinhole of the link plates of the train of knuckles in case of the silent chain. Further, because a large tensile force acts on the chain, a large surface pressure acts on the pins having the sliding contact movement.

[0018] While the invention relates to the chain pin, the aforementioned conventional pin and the manufacturing method thereof will be explained at first with reference to Fig. 1 before explaining the mode for carrying out the invention.

[0019] A base material 1 of the pin is made from steel such as high carbon steel for mechanical structures of S50C (C:0.47 to 0.53 %, Si:0.15 to 0.35 %, Mn:0.60 to 0.90 %, P:0.30 % or less, S:0.35 % or less, Cr as impurity: 0.20 % or less) for example and two steps of metal cementation processes are carried out on the pin base material (raw material) 1 of steel (Fe). The metal cementation process of the first step is a chrome cementation process (CrC cementation process, chromizing) in which powder containing Cr (metallic chrome) as penetrant raw material,  $Al_2O_3$  (alumina) as sintering stopping agent and  $NH_4Cl$  (ammonium chloride) as accelerator is put into a furnace together with the pin base material and temperature is raised to 800°C to 900°C, which is held for a predetermined time. In the CrC cementation process in the furnace, the following chemical reactions take place:

$\text{NH}_4\text{Cl} \rightarrow \text{NH}_3 + \text{HCl}$  (gas), and  $\text{HCl}$  (gas) + Cr (metallic powder)  $\rightarrow \text{CrCl}$  (gas) +  $\text{H}_2\uparrow$ . Then, in the  $\text{CrCl}$  atmosphere, Fe and C within the pin base material combine with Cr in the atmosphere, thus forming  $(\text{Fe}, \text{Cr})_x\text{Cy}$ , e.g.,  $(\text{Fe}, \text{Cr})_8\text{C}_7$ , and a coating layer on the surface of the pin base material 1 at first as chrome carbide ( $\text{CrC}$ ) penetrates therein.

[0020] After finishing the chrome cementation process of the pin base material, the pin whose surface is cemented and coated by the chrome carbide (chromizing pin) is taken out of the furnace once to carry out a vanadium cementation process (VC cementation process) as a metal cementation process of the second step. In the vanadium chrome cementation process,  $\text{FeV}$  (ferro-vanadium) is used as penetrant raw material. Beside that, alumina and ammonium chloride are put into the furnace together with the chromizing pin and the temperature is raised to  $900^\circ\text{C}$  to  $1,000^\circ\text{C}$ , which is held for a predetermined time similarly to the chrome cementation process described above. In the VC cementation process in the  $\text{VCl}$  atmosphere, C in the pin base material combines with V in the atmosphere, thus forming  $\text{VxCy}$ , e.g.  $\text{V}_8\text{C}_7$ , and a surface coating layer is formed on the layer of the chrome carbide on the surface of the pin base material as vanadium carbide penetrates therein. While the surface coating layer contains the vanadium carbide as its main component, it contains a small amount of the chrome carbide, thus forming a mixed layer.

[0021] Accordingly, in the conventional chain pin  $\text{P}_1$ , an intermediate layer 2 composed of the chrome carbide  $(\text{Fe}, \text{Cr})_8\text{C}_7$  is formed at first on the pin base material 1 mainly composed of Fe, and then a surface layer 3 mainly composed of vanadium carbide ( $\text{V}_8\text{C}_7$ ) is formed thereon as shown in FIG. 2. The intermediate layer 2 composed of the chrome carbide is clearly distinguishable from the pin base material 1 and the surface layer 3 mainly composed of vanadium carbide in a sectional photograph.

[0022] FIG. 3 shows an inventive manufacturing method of a chain pin. This manufacturing method is carried out by one step of metal cementation process, i. e., only a powder pack method of vanadium cementation process (VC compound cementation process). In the VC compound cementation process, powder containing  $\text{FeV}$  (ferro-vanadium) as penetrant (powder),  $\text{Al}_2\text{O}_3$  which is powder of refractory material as a sintering stopping agent and  $\text{NH}_4\text{Cl}$ , i.e., halide, such as ammonium chloride as additive (accelerator) is put into the furnace together with the pin base material 1. For the base material 1, steel members having a high chrome content (Cr: 0.6 wt% or more) such as chromium-molybdenum steel (SCM), chromium steel (SCr), nickel-chromium-molybdenum steel (SNCM), nickel-chromiumsteel (SNC), manganese-chromiumsteel (SMnC), high carbon chromium bearing steel (SUJ), nitriding steel (SACM, SCM, SCMV) and soft nitriding steel (SAC), e.g., SNCM439 (C:0.36 to 0.43 %, Si:0.15 to 0.35 %, Mn:0.60 to 0.90 %, P:0.030 % or less, S:0.03 % or less, Cr:0.6 to 1.00 %, Ni:1.6 to 2.00 %, Mo:0.15 to 0.30 %) or SUJ2 (C:0.95 to 1.10 %,

Si:0.15 to 0.30 %, Mn:0.50 % or less, P:0.025 % or less, 5:0.025 % or less, Cr:1.30 to 1.60 %) may be used. It is noted that SACM645, SCM56, SDMV2, SAC56 and SAC72 are preferable as the pin base material because they contain Cr by 1.00 [wt%] or more.

[0023] The temperature of the penetrant raw material and the pin base material is raised to  $1,000^\circ\text{C}$  to  $1,100^\circ\text{C}$  in the furnace and is quenched after holding that temperature for a predetermined time. Thereby, in the  $\text{VCl}$  atmosphere in which  $\text{HCl}$  (gas) decomposed from  $\text{NH}_4\text{Cl}$  combines with V in  $\text{FeV}$ , V in the atmosphere combines with Cr and C diffused from the pin base material (raw material) at first, thus forming compound carbide of vanadium and chrome  $[(\text{V}, \text{Cr})_x\text{Cy}$ , e.g.,  $(\text{V}, \text{Cr})_8\text{C}_7$ ]. Then, a boundary part composed of the vanadium and chrome compound carbide is formed on the surface of the pin base material. As the cementation process advances, the supply of Cr from the pin base material decreases (the supplying effect is reduced) and V in the atmosphere combines with C from the base material, thus forming vanadium carbide ( $\text{VxCy}$ , e.g.,  $\text{V}_8\text{C}_7$ ) that coats the surface of the pin.

[0024] FIGs. 4a through 4c show sections of the surface of the chain pin  $\text{P}_2$  manufactured by the inventive manufacturing method. The vanadium and chrome compound carbide  $[(\text{V}, \text{Cr})_8\text{C}_7]$  5 is formed in the boundary part facing to the pin base material 1 as described above. Further, the surface layer 6 composed of the vanadium carbide ( $\text{V}_8\text{C}_7$ ) is coated on the boundary part composed of the compound carbide 5. The compound carbide  $[(\text{V}, \text{Cr})_8\text{C}_7]$  diffuses also to the pin base material 1 because V penetrates therein and exists together with chrome carbide ( $\text{Cr}_8\text{C}_7$ ) therein. It also exists partly in the surface layer 6. Although it exists most in the boundary part with the pin base material 1, its Cr content decreases gradually from the interface 7 with the base material to the surface layer 6 and is not clearly divided. Accordingly, although the compound carbide  $[(\text{V}, \text{Cr})_8\text{C}_7]$  layer 5 may be assumed to exist in the boundary part from an analytical result of an X-ray probe micro-analyzer described later as shown in FIG. 4b, it is unable to recognize an interface 8 between the surface layer 6 and the compound carbide layer 5 and only the interface 7 between the pin base material 1 and the surface layer 6 is recognizable from a sectional photograph as shown in FIGs. 4a and 4c. Accordingly, it is unable to clearly divide the compound carbide layer 5.

[0025] FIGs. 5a and 5b show the results obtained by analyzing, through the use of the X-ray probe micro-analyzer, the inventive chain pin for which SUJ2 has been used as its base material and on which the above-mentioned vanadium cementation process has been carried out. FIG. 5a shows the vanadium content. While the vanadium content is about 80 % at a predetermined distance (about  $20 \mu\text{m}$ ) from the surface of the pin, it drops sharply at the boundary part 7 and is about 0 % in the pin base material.

[0026] FIG. 5b shows the chrome content analyzed by

the above-mentioned analyzer with a large current by using  $k\beta 1$  primary ray. It is understood from the analysis that the chrome content drops gradually from the base material to the surface of the pin. That is, chrome (Cr) diffuses and penetrates into the vanadium carbide layer (surface layer) from the chrome-rich pin base material by the heat treatment at high temperature, thus forming the compound carbide layer  $[(V, Cr)_8C_7]5$ . The chrome content within the compound carbide layer is highest at the interface 7 and decreases gradually toward the surface of the pin. The content is about 0 [%] at a predetermined distance (about 6  $\mu m$ ) from the interface. The part from there to the surface of the pin is the surface layer 6 mostly composed of the vanadium carbide.

[0027] Generally, the heat treatment temperature has been set at 1,000°C or less in the vanadium cementation process in order to avoid the grain of the vanadium carbide from being roughened and the temperature has been set at 900°C to 1,000°C also in the conventional vanadium cementation process shown in FIG. 1. Even if carbide forming elements, e.g., Cr, exists in the pin base material, its content as well as diffusion effective amount are small in the conventional method. Therefore, it is difficult to obtain the composition gradient intermediate layer like the compound carbide layer  $[(V, Cr)_8C_7]5$  described above. Even if it may be possible to obtain the diffusion effect of the carbide forming element such as Cr contained in the base material by increasing the heat treatment temperature to 1,000°C or more, it is unable to obtain the diffusion effect described above because the amount of the carbide forming element (Cr) in the base material is small as described above.

[0028] However, the invention enables one to obtain the composition gradient intermediate layer composed of the above-mentioned compound carbide by diffusing Cr in the base material to the vanadium carbide layer by setting the temperature of the vanadium cementation process at 1,000°C or more because the Cr content in the base material is high. It is noted that the temperature of the cementation process is desirable to be in a range from 1,000°C to 1,100°C because the vanadium carbide (VC) grain is roughened, possibly causing a fall-out phenomenon of the VC grains, if the temperature of the heat treatment exceeds 1,100°C.

[0029] While the chain pin P2 has the surface treated coating film, i.e., the coating film in which the surface layer 6 composed of  $V_8C_7$  is combined with the boundary part 5 composed of  $(V, Cr)_8C_7$ , of 10  $\mu m$  to 30  $\mu m$ , it is preferable to be around 20  $\mu m$  (16 to 25  $\mu m$ ). Then, a predetermined quenching, tempering or isothermal transformation process is carried out after the cementation process described above in order to enhance the pin.

[0030] Although the conventional manufacturing method of the pin P1, described above has required two steps of heat treatments as shown in FIG. 1 and has been cumbersome that much, the inventive manufacturing method of the pin P2 requires only one step of heat treatment as shown in FIG. 3. Accordingly, the high precision

pin P2 may be manufactured readily, effectively and accurately.

[0031] Further, although the chrome carbide ( $Cr_8C_7$ ) in the intermediate layer adheres the surface layer 3

5 mainly composed of vanadium carbide ( $V_8C_7$ ) to the base material (Fe) at high adhesion strength in the conventional chain pin P1, the distinguishable interfaces 2a and 2b exist between the chrome carbide layer 2 and the surface layer 3 and the adhesion strength is not enough 10 because the chrome carbide layer (intermediate layer) 2 is composed of clearly distinguishable independent layer as shown in FIG. 2.

[0032] However, in the inventive chain pin P2, the compound carbide  $[(V, Cr)_8C_7]$  is formed by Cr and C supplied

15 from the chrome-rich base material 1 together with V in the atmosphere, the compound carbide layer 5 is undistinguishable in the boundary part between the surface layer 6 composed of vanadium carbide ( $V_8C_7$ ) and the pin base material 1 and the Cr content changes gradually 20 as shown in FIGs. 4a, 4b and 4c, so that the compound carbide 5 adheres the surface layer 6 composed of vanadium carbide ( $V_8C_7$ ) to the pin base material 1 with high adhesion strength. Further, the surface layer 6 composed of vanadium carbide has high face pressure 25 resistance and prevents peeling from occurring at the surface even in a severe use condition in which high face pressure acts under a high-temperature environment.

[0033] FIG. 6 shows results of scratch test carried out to find peeling critical load by scratching the pins while

30 pressing a diamond indenter thereto and increasing the load continuously. The test results show that the pin P2 manufactured through the inventive compound cementation process has high peeling critical load as compared to the conventional pin P1. That is, it is understood that 35 vanadium carbide, i.e., the surface layer, of the inventive pin P2 is adhering strongly as compared to the conventional pin P1.

#### Industrial Applicability

40 [0034] The inventive chain pin described above is applicable to all kinds of power transmission chains such as publicly known roller chains and silent chains and is suitably applicable to a timing chain or the like used in a 45 severe use environment such as an engine.

#### Claims

50 1. A chain pin characterized in that:

compound carbide of vanadium and chrome exists in a boundary section between a pin base material and a surface layer composed of vanadium carbide; and

55 a content of chrome in said compound carbide decreases gradually toward said surface layer.

2. The chain pin as set forth in Claim 1, wherein said chain pin is a pin for use in a silent chain.

3. The chain pin as set forth in Claim 1, wherein said chain pin is a pin for use in a roller chain.

4. A manufacturing method of a chain pin **characterized in that:**

steel containing more than 0.6 [%] of chrome is used as a pin base material; and a cementation process is carried out on said pin base material at predetermined temperature within a gaseous atmosphere containing vanadium; wherein said cementation process comprising steps of:

forming, at first, compound carbide of vanadium and chrome on the surface of said pin base material by chrome and carbon supplied from said pin base material and vanadium within said atmosphere; and forming then a surface layer composed of vanadium carbide by vanadium within said atmosphere in a condition in which the supply of chrome from said pin base material decreases without forming an interface between said compound carbide.

5. The manufacturing method of the chain pin as set forth in Claim 4, wherein said cementation process comprises a powder pack method using powder containing vanadium as a penetrant rawmaterial, a sintering stopping agent and an accelerator, and the temperature of the heat treatment is set at 1,000 [°C] to 1,100 [°C].

6. The chain pin manufacturing method as set forth in Claim 4, wherein said chain pin is a pin for use in a silent chain.

7. The chain pin manufacturing method as set forth in Claim 4, wherein said chain pin is a pin for use in a roller chain.

2. The chain pin as set forth in Claim 1, wherein said chain pin is a pin for use in a silent chain.

3. The chain pin as set forth in Claim 1, wherein said chain pin is a pin for use in a roller chain.

4. A manufacturing method of a chain pin **characterized in that:**

steel containing 0.6 to 3.3 [%] of chrome is used as a pin base material; and a cementation process is carried out on said pin base material at predetermined temperature within a gaseous atmosphere containing vanadium; wherein said cementation process comprising steps of:

forming, at first, compound carbide of vanadium and chrome on the surface of said pin base material by chrome and carbon supplied from said pin base material and vanadium within said atmosphere; and forming then a surface layer composed of vanadium carbide by vanadium within said atmosphere, in a condition in which the supply of chrome from said pin base material decreases, without forming an interface between said compound carbide.

5. The manufacturing method of the chain pin as set forth in Claim 4, wherein said cementation process comprises a powder pack method using powder containing vanadium as a penetrant raw material, a sintering stopping agent and an accelerator, and the temperature of the heat treatment is set at 1,000 [°C] to 1,100 [°C].

6. The chain pin manufacturing method as set forth in Claim 4, wherein said chain pin is a pin for use in a silent chain.

7. The chain pin manufacturing method as set forth in Claim 4, wherein said chain pin is a pin for use in a roller chain.

### **Amended claims under Art. 19.1 PCT**

- 1. A chain pin characterized in that:**

compound carbide of vanadium and chrome exists in a boundary part between a pin base material containing 0.6 to 3.3 [%] of chrome and a surface layer composed of vanadium carbide; and a content of chrome in said compound carbide decreases gradually toward said surface layer.

**Statement under Art. 19.1 PCT**

- 50 1. In Claims 1 and 4 which are independent claims, changes are made so as to restrict the pin base material to contain 0.6 to 3.3 [%] of chrome.

55 2. Claims 2 and 3 and 5 through 7 which are dependent claims are not changed.

55 3. The lower limit of 'chrome content of "0.6 %"' is disclosed in Paragraph [0008] and others.

The base of the upper limit of chrome content of "3.3 %" is "SCM 56" that is cited as a preferable material for the pin base material in Paragraph [0022].

That is, SCM56 is an item name (symbol) of Daido Steel Co., Ltd. and its chemical component is described, as specific components, as C: 0.25, Mn: 0.5, Cr: 3.2 and Mo: 0.5 in the handbook of Daido Steel Co., Ltd.

The component of SCM 56 coincides almost with a component range of "31CrMo12" which is a steel type name in the ISO specifications of nitriding steel provided in JIS G7502 and 31CrMo12 is provided to contain Cr: 2.80 to 3.30. An allowable fluctuation value between the provided analytical value and a product analytical value of Cr is  $\pm 0.10$ .  
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Therefore, although the upper limit of the Cr content of SCM 56 is  $3.30 + 0.10 = 3.40$  when 31CrMo12 is taken into account, the specified upper limit becomes 3.3 [%] because SCM 56 is described as to contain 3.2 as its specific component and the allowable fluctuation value of 0.10 is added to that as a steady value.  
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FIG.1

**PRIOR ART METHOD**

**PENETRANT RAW MATERIALS**

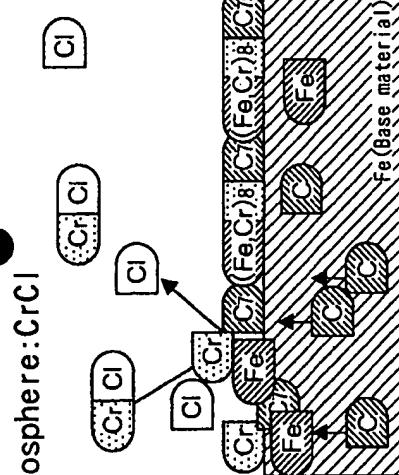
- FeV (ferro-vanadium) or Cr (metallic chrome)
- Al<sub>2</sub>O<sub>3</sub> (alumina)
- NH<sub>4</sub>Cl (ammonium chloride)

**Heat Treatment Temperature**

CrC chromo  
cementation process:  
800°C to 900°C

**Requires Two Steps  
and Long Processing Time**

VC cementation process:  
900°C to 1,000°C



**Atmosphere: VCI**

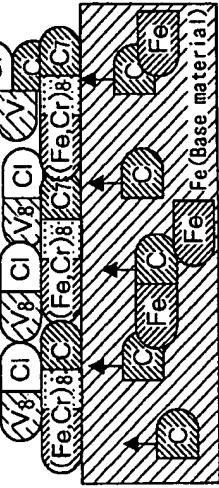


FIG.2

STRUCTURE OF COATING FILM

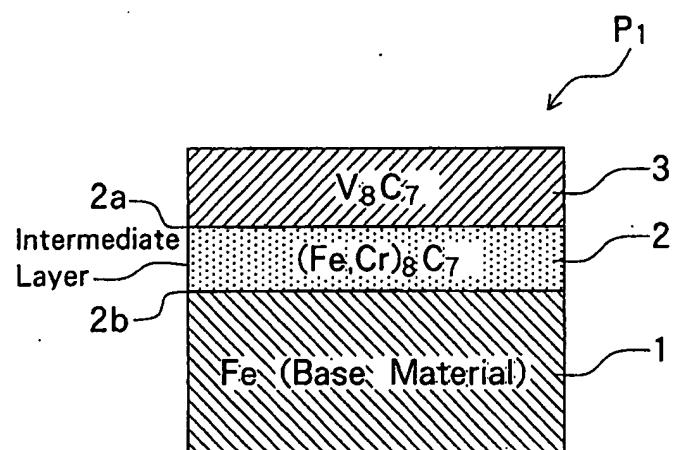


FIG.3

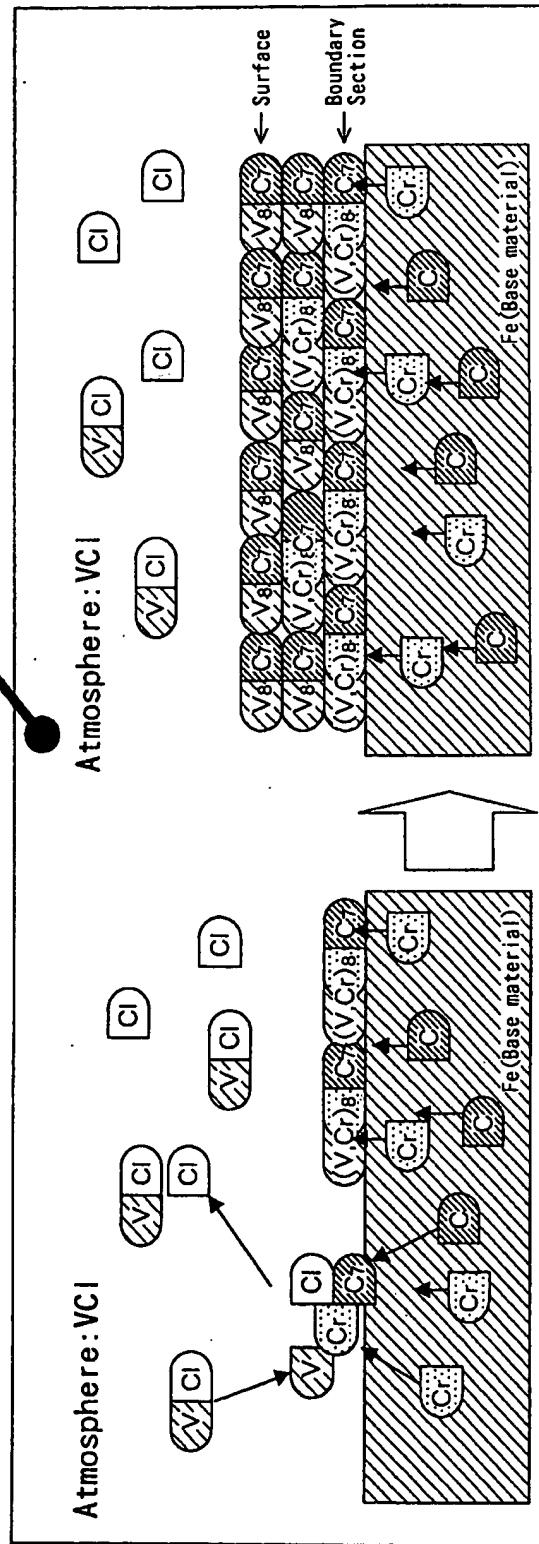
**INVENTIVE METHOD**

**PENETRANT RAW MATERIALS**

- FeV (ferro-vanadium)
- Al<sub>2</sub>O<sub>3</sub> (alumina)
- NH<sub>4</sub>Cl (ammonium chloride)

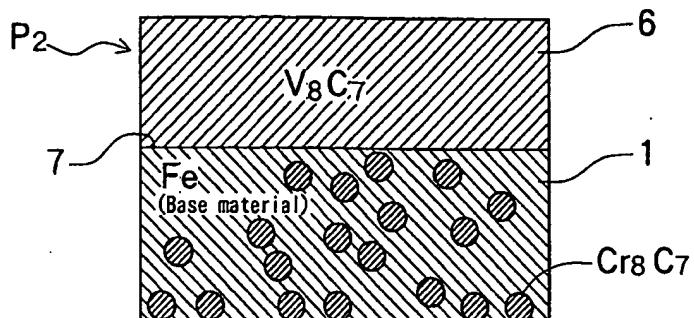
**Heat Treatment Temperature**

VC compound  
cementation process:  
1,000°C to 1,100°C

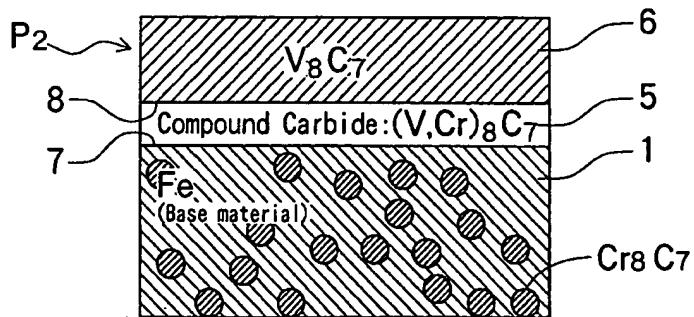


**FIG.4a**

STRUCTURE OF COATING FILM (SEEN BY PHOTOGRAPH)

**FIG.4b**

STRUCTURE OF COATING FILM (FROM ANALYSIS)

**FIG.4c**

SCHEMATIC SECTION VIEW

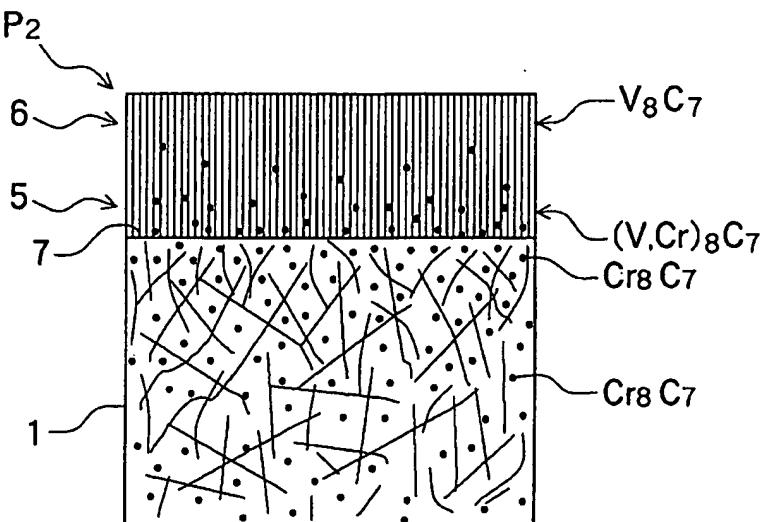


FIG.5a

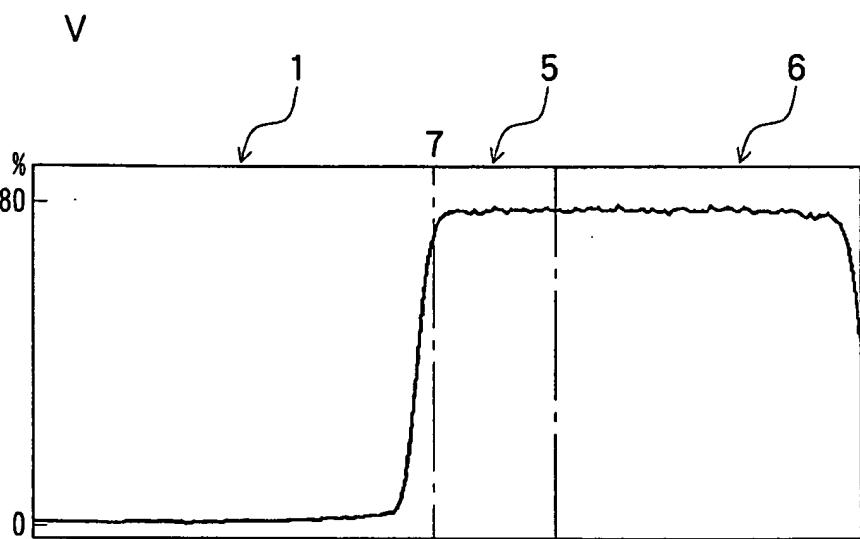


FIG.5b

Cr

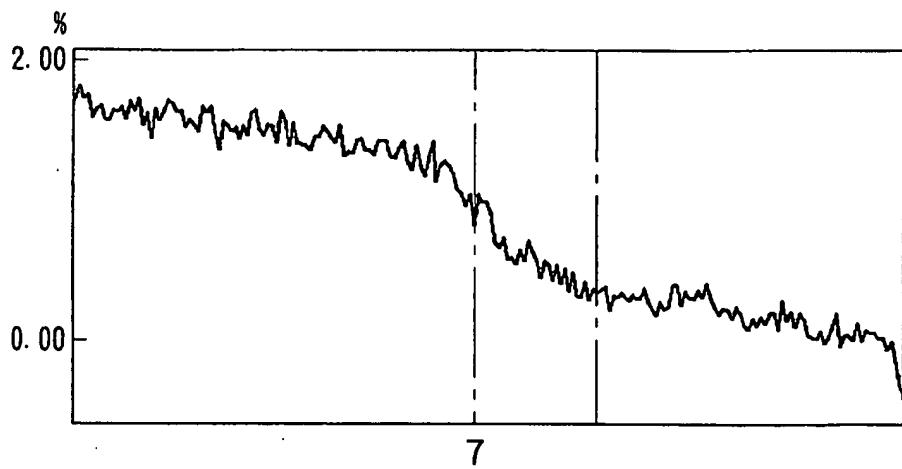
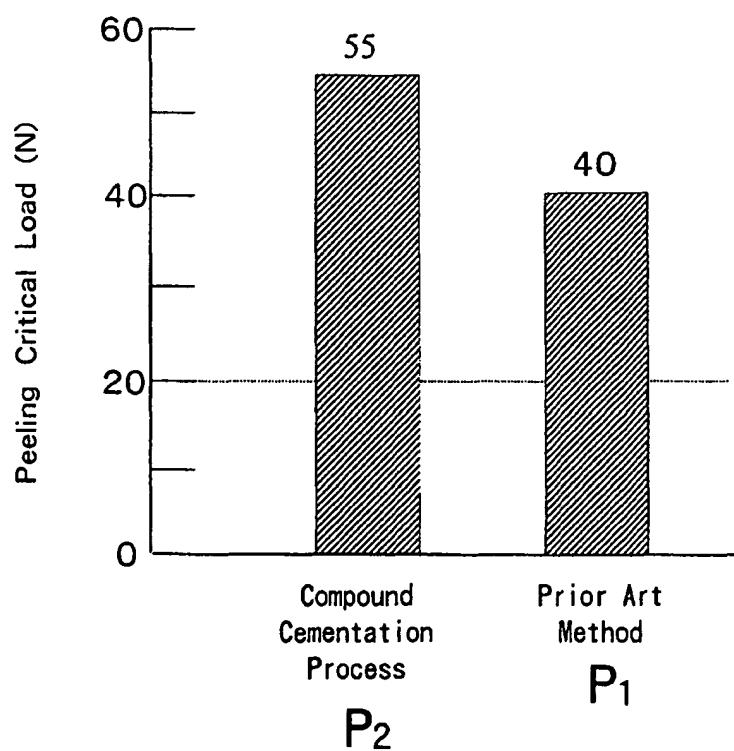


FIG.6

RESULT OF SCRATCH TEST



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2004/007511

A. CLASSIFICATION OF SUBJECT MATTER  
Int.Cl<sup>7</sup> F16G13/06, C23C10/36

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
Int.Cl<sup>7</sup> F16G13/06, C23C10/36Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  
Jitsuyo Shinan Koho 1922-1996 Toroku Jitsuyo Shinan Koho 1994-2004  
Kokai Jitsuyo Shinan Koho 1971-2004 Jitsuyo Shinan Toroku Koho 1996-2004

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 02/2843 A2 (BORG WARNER, INC.), 10 January, 2002 (10.01.02), Par. Nos. [0009] to [0035]; Fig. 3 & JP 2004-502033 A Par. Nos. [0013] to [0047]; Fig. 3 & US 2002/31687 A1	1-7
A	JP 2002-195356 A (Borg-Warner Automotive, Inc.), 10 July, 2002 (10.07.02), Full text & US 2002/119852 A1	1-7

 Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "B" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family
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Date of the actual completion of the international search 14 July, 2004 (14.07.04)	Date of mailing of the international search report 03 August, 2004 (03.08.04)
Name and mailing address of the ISA/ Japanese Patent Office  Facsimile No.	Authorized officer  Telephone No.

Form PCT/ISA/210 (second sheet) (January 2004)